Vibrational Decoupling of Rings in Amorphous Solids

F. L. Galeener, R. A. Barrio,(a) E. Martinez,(b) and R. J. Elliott(c)
Xerox Palo Alto Research Center, Palo Alto, California 94304

(Received 4 October 1984)

It has been proposed that the sharp Raman lines seen in vitreous SiO_2 and other glasses are the signatures of *highly regular* rings of bonds connected into a more disordered network. We derive a condition for vibrational decoupling of the appropriate ring modes from the surrounding network, and thereby explain both the anomalously narrow linewidths and the absence of Si isotope shifts. The results encourage the development of vibrational spectroscopy as a probe of intermediate-range order in the form of regular rings in amorphous solids.

PACS numbers: 63.50.+x, 61.40.Df

The vibrational spectra of amorphous (a-) solids consist primarily of broad lines, whose width has been ascribed to disorder in the bond angles[1-3] and force constants[4] and to "breakdown" in vibrational selection rules.[5] Recently, however, attention has been drawn to significantly narrower lines which are also part of the Raman spectra of several vitreous (v-) materials, including v-SiO_2,[6] v-B_2O_3,[7] v-As_2O_3,[8] and v-$GeSe_2$.[9] It has been proposed[6] that most of these sharp lines are due to intermediate-range order[10] in the form of highly regular rings of bonds. In this Letter, we demonstrate very simply *how* such ring modes can decouple vibrationally from the rest of the network, giving Raman lines with the observed sharpness and other properties. Elsewhere[11] we will present Green's-function calculations[3] on rings terminated by Bethe lattices[12] (BL) appropriate for v-SiO_2.

Consider, for example, the polarized Raman spectra of v-SiO_2 shown in Fig. 1. The broad features at 420, 800, 1065, and 1200 cm^{-1} can be understood in terms of the vibrations of a continuous "random" network as described in detail by several authors.[1-4,12] The two sharp lines ($D_1 = 495$ cm^{-1} and $D_2 = 606$ cm^{-1}) have been ascribed to a large variety[10] of wrong-bond or broken-bond defects. Galeener[6,10] has argued that each of these models contradicts recent experiments and that the observed properties of the sharp lines are better explained in terms of the breathing modes of regular rings (which will show *little* electrical activity). D_2 was assigned to the breathing mode of a planar 3-ring, and D_1 to that of a regular but slightly puckered 4-ring.[6] The planar 3-ring is depicted schematically in Fig. 2. (Since the O-Si-O angle is assumed to be tetrahedral,[6] $\phi = 109.5°$ and $\theta = 130.5°$).

The ring assignments in v-SiO_2 were made *partly* on the basis of nearly exact agreement with the dominant Raman frequencies of isolated cyclosiloxane ring molecules.[10] How can such a breathing mode be so little shifted or broadened when the

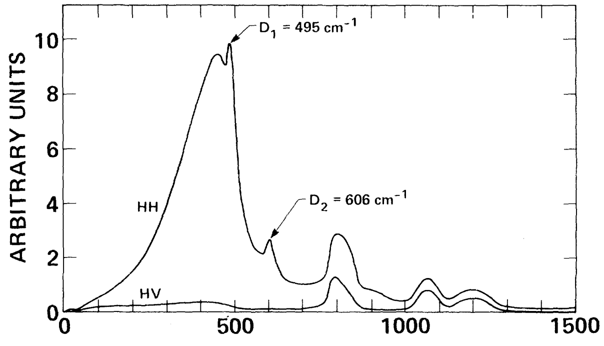

FIG. 1. The polarized Raman spectra of v-SiO_2, showing the sharp defect lines D_1 and D_2 which have been ascribed to various wrong bonds, or broken bonds, *or* to regular rings of Si–O bonds embedded in an otherwise more disordered network.

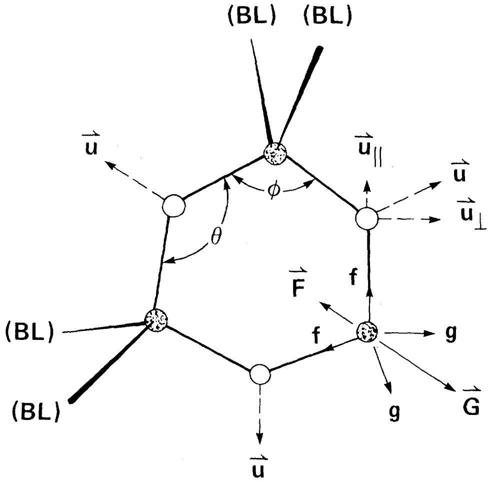

FIG. 2. The breathing mode of the 3-ring assigned to D_2 in Fig. 1. When the net "central" force $\vec{F}$ on each Si atom is cancelled by the net "noncentral" force $\vec{G}$, the Si atoms are motionless, the mode is vibrationally decoupled from the rest of the network, and there is no Si isotope shift (for this mode).

ring is connected into the disordered v-SiO$_2$ network? At an extreme, the ring model has been rejected[13–15] on the basis[14] that "small units, embedded in a dense medium, can never give rise to narrow vibrational lines... a consequence of the uncertainty principle." In fact, sharp resonances from impurity modes are well known in crystals when the impurities involved are *weakly* coupled to the rest of the lattice.[16] We now show that a regular ring which is *strongly bonded* into the network can have vibrational modes whose *motion is weakly coupled;* so that sharp lines are both possible and likely, even in an otherwise disordered solid.

Consider the planar 3-ring in Fig. 2. It is connected to the rest of the network by six Si–O bonds (four of them shown and labeled BL in Fig. 2). In the breathing mode of the ring all three O atoms move in phase along the bisectors of ϕ (the dashed lines in Fig. 2). In general, these O displacements will exert forces on the Si atoms, which will communicate their motion to the rest of the network by distorting the BL bonds: This will broaden the breathing-mode frequency, in a way that we shall calculate later. On the other hand, if there happens to be zero *net* force on the Si atoms they will remain stationary, and the O motion in the ring will *not* be coupled to the network.

It is easy to derive a condition for such decoupling in terms of the Born force constants α and β, where α measures the "central" (or bond-length restoring) force and β the "noncentral" (or bond-orientation restoring) force. Other force-constant models can be used,[11] but the Born forces are the most common and successful in modern work on disordered solids.[1–3,12,17] The individual central ($\vec{f}$) and noncentral ($\vec{g}$) forces acting on a Si atom are shown in the lower right of Fig. 2. In the absence of Si motion the magnitudes of these forces are given by $f=\alpha' U_{\parallel}=\alpha' u\cos(\theta/2)$ and $g=\beta' u_{\perp}=\beta' u\sin(\theta/2)$, where the prime denotes the force constant for a bond *within* the ring. The magnitudes of the oppositely directed *total* central ($\vec{F}$) and noncentral ($\vec{G}$) forces acting on the Si atom are then given by $F=2f\cos(\phi/2)$ and $G=2g\sin(\phi/2)$. The *absence* of Si motion requires $F=G$, so that perfect decoupling occurs when α'/β' has the value

$$(\alpha'/\beta')_d=\tan(\theta/2)\tan(\phi/2). \tag{1}$$

The angular frequency at perfect decoupling is easily shown[11] to be

$$\omega_d^2=(\alpha'/m)[(1+\cos\theta)+(\beta'/\alpha')_d(1-\cos\theta)], \tag{2}$$

where m is the mass of the O atom. In the special case of the planar 3-ring in Fig. 2 ($\phi=109.5°$; $\theta=130.5°$), one has

$$(\beta'/\alpha')_d=0.326 \tag{3}$$

and

$$\omega_d^2=0.888(\alpha'/m). \tag{4}$$

In v-SiO$_2$, the breathing mode of the 3-ring has been assigned[6] to $D_2=606$ cm^{-1}. When one assumes perfect decoupling at this frequency, Eqs. (3) and (4) require[18] that the *ring* force constants be $\alpha_d'=390$ N/m and $\beta_d'=127$ N/m. These values are very close to those that fit the breathing mode of the hexamethylcyclotrisiloxane molecule, and compare appropriately with the values of α and β deduced for the host network, as next described.

Reference 3 shows that the broad *network* features in Fig. 1 are well fit with a dihedral-angle-(δ-)averaged Bethe lattice having $\alpha=507$ N/m, $\beta=78$ N/m, and a most probable Si-O-Si angle $\langle\theta\rangle=154°$. The substantial differences in force constants between the BL network and the 3-ring are to be expected,[19,20] because θ in the ring (130.5°) is significantly smaller than $\langle\theta\rangle$ in the network ($\sim 152°$). Theoretical calculations of bonding energy versus θ for a Si-O-Si bridge[19] indicate that the changes *are* in the expected directions: as θ decreases from BL to 3-ring, the Si-O bond length *increases* and the stretching force constant α is substantially reduced; simultaneously, the Si-Si distance *decreases,* Si-Si repulsions grow, and the angular restoring forces (hence β) are appreciably enlarged.[20]

We have studied[11] the tolerance for *imperfect decoupling.* The network outside the $n=3$ ring in Fig. 2 was replaced by six of the above δ-averaged Bethe lattices,[3] and the ring dynamics were computed for a range of β'/α' on either side of perfect decoupling. This is an adaptation of the cluster BL method of Laughlin and Joannopoulos.[12] Since greater realism in the model can only *increase* the calculated linewidth ΔW, we will reject all parameter sets leading to ΔW greater than the observed[6] D_2 linewidth of 30 cm^{-1}. Some examples of computed Raman response are given in Fig. 3.

When the internal ring parameters α', β' are the *same* as those for the host Bethe lattice, one obtains Fig. 3(b), where the dominant Raman line of the ring is not quite at the correct frequency and is clearly too wide.

When the perfect decoupling parameters are used, one obtains Fig. 3(c) in which a single mode is dominant at 606 cm^{-1} and is of zero width. (The

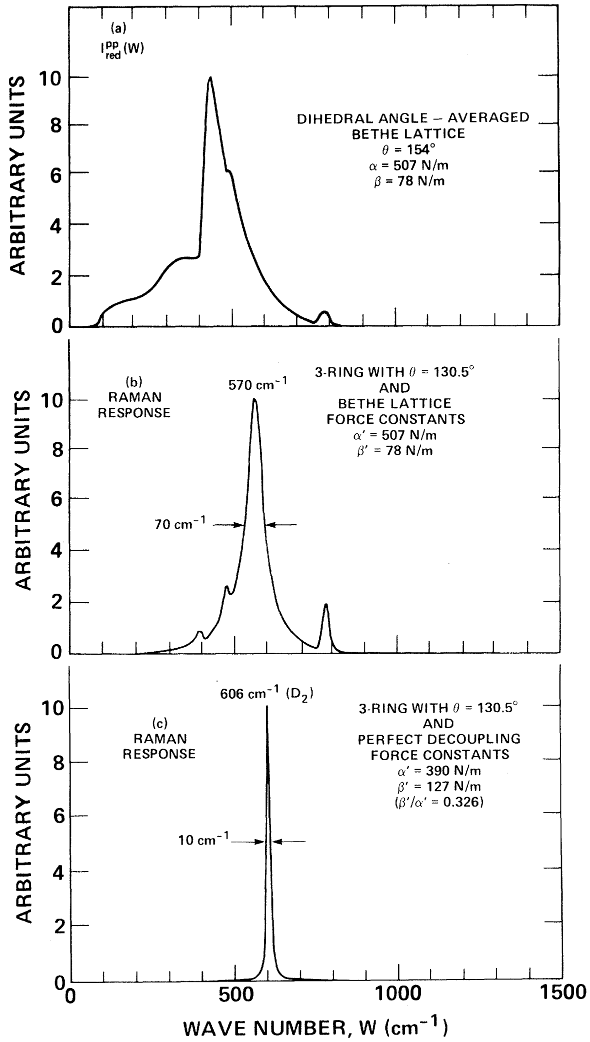

FIG. 3. The calculated Raman response ($HH-\frac{4}{3}\times HV$) for (a) the Bethe lattice that represents the v-SiO$_2$ host network; (b) the 3-ring when the ring force constants are the same as for the host network; and (c) the 3-ring when the ring force constants satisfy the perfect decoupling condition [Eq. (1)]. In (c), the ring response is a single narrow highly polarized line showing no Si isotope shift [as is observed (Refs. 6 and 10) at $D_2=606$ cm^{-1}].

10-cm^{-1} width shown is an additive artifact of the method of avoiding singularities in the computations.) This O breathing mode *contains no Si motion* and will therefore show no Si isotope shift, as is observed[21] for both D_2 and D_1.

Figure 4 shows the 3-ring linewidth as a function of β'/α', with α' adjusted to keep the peak at 606 cm^{-1}. We conclude that β'/α' can vary between 0.20 and 0.56 and still predict a linewidth below the observed value ($40-10=30$ cm^{-1}). The decoupling condition is thus not very stringent, and it is *reasonable* to believe that chemical bonding has provided a ratio of central to noncentral forces that allows for adequate decoupling of the ring breathing mode.

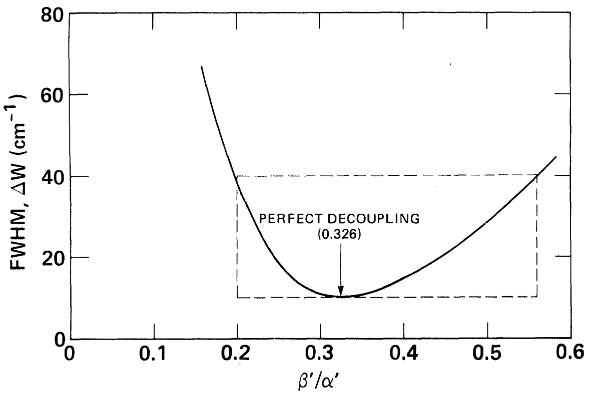

FIG. 4. The calculated linewidth ΔW for the Bethe-lattice-terminated 3-ring, showing that the decoupling condition is not stringent. That is, ΔW is less than or equal to observation ($40-10=30$ cm^{-1}) over a large range of force-constant ratios ($0.2\leq\beta'/\alpha'\leq0.56$).

When the angular forces (β) of the Born model are replaced by the more realistic ones of the *simple* valence force field,[22] perfect decoupling is still easily achieved.[11] If the length-angle interactions of the *generalized* valence force field[22] are introduced, perfect decoupling may not be possible, but such forces are so weak that adequate decoupling is still assured.

The case of regular 4-rings has been treated in a similar way.[11] Perfect decoupling of a *planar* 4-ring is also described by Eqs. (1) and (2), with $\phi=109.5°$ and $\theta=160.5°$,[6] but this leads to unrealistic force constants in order to fit the $D_1=495$ cm^{-1} frequency. On the other hand, a regular *puckered* "oxygen boat" 4-ring perfectly decouples at $D_1=495$ cm^{-1} with θ set at the most probable angle (154°), $\phi=109.5°$, $\alpha'_d=467$ N/m, and $\beta'_d=97$ N/m. These force constants are very close to the BL parameters. The calculated allowable range of β'/α' is still greater than that for the 3-ring, making adequate decoupling extremely likely, *even when the ring is slightly irregular.* This *dynamical* requirement that the 4-ring be puckered agrees with the experimental fact[23] that the isolated cyclosiloxane 4-ring is nonplanar.

Higher-order rings ($n\geq5$) are not expected to be regular in v-SiO$_2$, as discussed in Ref. 6; the consequent spread in values of θ will produce strong coupling of motion to the network, and a wide range of frequencies. Such responses contribute to the *broad* features in Fig. 1.

It has thus been demonstrated that *certain modes* of regular rings of A-X bonds in an AX_2 tetrahedral glass can be vibrationally decoupled from the rest of the network to which the rings are *strongly* attached. This decoupling can also be realized in crystals and molecules, since it is accomplished by a near cancellation of central and noncentral forces *within the ring* acting on the high-coordination (Si) atoms that connect to the network. Therefore the connecting atoms do not move during the ring vibration, and this explains the absence of mode isotope shift when isotopic substitution is carried out on the connecting (Si) atoms. These modes are *highly localized!* The perfect decoupling condition [Eq. (3)] need not be satisfied exactly and can be expected to be adequately met in many network glasses —opening the way to study of this form of intermediate-range order by vibrational spectroscopy.

The authors are grateful for support of this work by the U.S. Navy Office of Naval Research. Three of us (R.A.B., E.M., and R.J.E.) wish to thank Xerox Palo Alto Research Center for its hospitality during their visits. One of us (F.L.G.) is indebted to the Cavendish Laboratory, University of Cambridge, and to Dr. W. A. Phillips for generous support during the preparation of the manuscript.

---

[a] Permanent address: Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apdo. Postal 70-360, México 20 Distrito Federal, México.

[b] Permanent address: Departamento de Física Fundamental, Universidad Autónoma de Madrid, Madrid, Spain.

[c] Permanent address: University of Oxford, Department of Theoretical Physics, 1 Keble Road, Oxford OX1 3NP, United Kingdom.

[1] R. J. Bell, in *Excitations in Disordered Systems,* edited by M. F. Thorpe (Plenum, New York, 1982), p. 333ff and p. 347ff.

[2] F. L. Galeener, Phys. Rev. B **19**, 4292 (1979).

[3] R. A. Barrio, F. L. Galeener, and E. Martinez, Phys. Rev. Lett. **52**, 1786 (1984).

[4] R. M. Martin and F. L. Galeener, Phys. Rev. B **23**, 3071 (1981).

[5] R. Shuker and R. W. Gammon, Phys. Rev. Lett. **25**, 222 (1970).

[6] F. L. Galeener, Solid State Commun. **44**, 1037 (1982).

[7] D. L. Griscom, in *Borate Glasses,* edited by L. D. Pye, V. D. Frechette, and N. J. Kreidl (Plenum, New York, 1978), p. 11ff.

[8] G. Lucovsky, C. K. Wong, and W. B. Pollard, in *The Structure of NonCrystalline Materials 1982,* edited by P. H. Gaskell, J. M. Parker, and E. A. Davis (Taylor and Francis, London, 1983), p. 369.

[9] P. M. Bridenbaugh, G. P. Espinosa, J. E. Griffiths, J. C. Phillips, and J. P. Remeika, Phys. Rev. B **20**, 4140 (1979).

[10] F. L. Galeener, in Ref. 8, p. 337.

[11] F. L. Galeener, R. A. Barrio, E. Martinez, and R. J. Elliott, to be published.

[12] R. B. Laughlin and J. D. Joannopoulos, Phys. Rev. B **16**, 2942 (1977).

[13] J. C. Phillips, Solid State Phys. **37**, 93 (1982).

[14] J. C. Phillips, J. Non-Crystall. Solids **63**, 347 (1984).

[15] J. C. Phillips, Bull. Am. Phys. Soc. **29**, 296 (1984).

[16] See, e.g., K. Lakatos and J. A. Krumhansl, Phys. Rev. **175**, 841 (1968).

[17] P. N. Sen and M. F. Thorpe, Phys. Rev. B **15**, 4030 (1977).

[18] Equation (4) is $W_d^2 = (1.51\times10^4\ \mathrm{cm}^{-2}\ \mathrm{u\ m\ N}^{-1})\alpha'/m$.

[19] M. D. Newton and G. V. Gibbs, Phys. Chem. Minerals **6**, 221 (1980).

[20] G. V. Gibbs, private communication.

[21] F. L. Galeener and A. E. Geissberger, Phys. Rev. B **27**, 6199 (1983).

[22] For definition, see J. R. Ferraro and J. S. Ziomek, *Introductory Group Theory* (Plenum, New York, 1969), p. 130.

[23] H. Steinfink, B. Post, and I. Fankuchen, Acta Crystallogr. **8**, 420 (1955).